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THERMAL EFFUSIVITY AS A NON-DESTRUCTIVE METHOD TO CHARACTERIZE THIN FILMS

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Mathis Instrument's Thermal Conductivity Probe (TC Probe®) offers a potential non-destructive method for looking at changes in a 3- to 5-mil polymer coating. The TC Probe is based on a modified hot wire technique, operating under constant current conditions. The temperature of the heating element is monitored during sample testing, and changes in the temperature at the interface between the probe and sample surface, over the testing time, are continually measured. Because the coatings are thin, the potential for heat transfer into the substrate is a potential problem. Care must be taken to assure that the analysis time is set to eliminate or at least minimize thermal penetration. The effusivity is a function of the density, heat capacity, and thermal conductivity. As a polymer coating degrades as a result of environmental exposure, the structure of the polymer changes. Chain scission reduces molecular weight and shorter polymer chains become more mobile. Resulting changes in the polymer density and thermal conductivity can be observed using the TC Probe.

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INTRODUCTION

The military uses polymer coatings on all tactical vehicles and aircraft to protect against corrosion, as well as for camouflage and stability against nuclear and biological decontamination. These coatings are subjected to an extreme variation in temperature and humidity, as well as exposure to ultraviolet light. Environmental degradation results in the loss of coating appearance, blistering, peeling, and surface corrosion. The resulting maintenance costs and lack of materiel readiness is a critical problem for our military preparedness. Non-destructive methods to detect coating degradation can help to predict when a coating has failed and needs to be reapplied. A modified hot wire technique has the potential to do this.

The modified hot wire technique (ref 1) is a transient heat reflectance method that is similar to the hot wire method having the heating element supported on one side of the backing, which allows for the heat flow in only one direction. This eliminates the intrusive nature of the heating element and allows solids to be tested without melting. The heating element is placed in intimate contact with the surface of a flat sample with a minimum dimension of 5 × 25 mm. The heating element is operated at constant temperature during the test and the change in surface temperature measured. The temperature change of the element is inversely proportional to the ability of the sample to transfer heat. From this relationship and calibration with certified standards, the effusivity can be measured. Heat is generated in the sensor and dissipates into the material being tested. The temperature of the heating element is monitored and plotted over time. In this application, the heat wave passes through the coating and into the substrate.

The technique is interfacial; heat is applied and measured on the same surface. This is advantageous for analyzing a coating surface that is a complex mixture of polymers, solvents, additives, pigments, and extenders. However, the measurement is complicated because the coatings are thin (75–125 μm) and testing parameters must be adjusted to minimize substrate penetration.

The thermal conductivity probe measures the effusivity of a material, which is (ref 2):

$$\text{Effusivity} = (\kappa \rho c_p)^{1/2}$$

where κ is the thermal conductivity (w/m K), ρ is the density (kg/m^3) and c_p is the heat capacity (J/kg K). The probe head is placed in intimate contact with a material surface, the sensor emits a constant heat and the temperature rise at the surface is monitored. Materials that conduct heat readily produce a lower rate of temperature rise because heat is conducted away from the surface. Conversely, materials that are insulators conduct heat poorly and the temperature rises substantially at the surface (ref 3).

Polymer shim stock pieces, ranging from 0.003 to 0.005 in. (7.62 to 12.7 μm), were placed over aluminum standard Q test panels and the effusivity measured at each thickness. The procedure was repeated using various heating cycles. The data were compared to determine at what point and to what degree the heat wave penetrated the coating and entered the substrate.

The Mathis Thermal Conductivity Probe (TC Probe®) provides a potential method for monitoring the extent of degradation to a polymer coating that is quick and non-destructive. The polymer density, heat capacity, and thermal conductivity can change as the polymer degrades or the adhesion can be affected by substrate corrosion or pitting, which can result in changes in the effusivity. The potential to test materials and products for coating delamination and degradation in the field without sample preparation makes this an interesting method.

EXPERIMENTAL METHOD

The Mathis TC Probe was used to measure the effusivity. The samples were placed on top of the probe (see Figure 1) and a 2.36-kg mass was set on the samples to ensure that they were in intimate contact with the probe surface (ref 4). The samples ranged from an aluminum substrate to plastic shim/substrate to an aluminum substrate with a chemical conversion coating, epoxy primer, and polyurethane top coat. The test duration was varied from 0.2 to 5.0 seconds, the start time was varied from 0.05 to 1.00 second, and the sample sampling rate and cooling time were held constant at 400 Hz and 2.0 minutes, respectively. This unusually short test duration was used because the heat wave penetrated through the thin polymer coating (75–100 μm). Consequently, the test parameters had to be adjusted to minimize or prevent the heat penetration into the substrate. Penetration of heat through the coating can, however, yield information relating to the coating/substrate interface, such as delamination, pitting, and substrate oxidation.

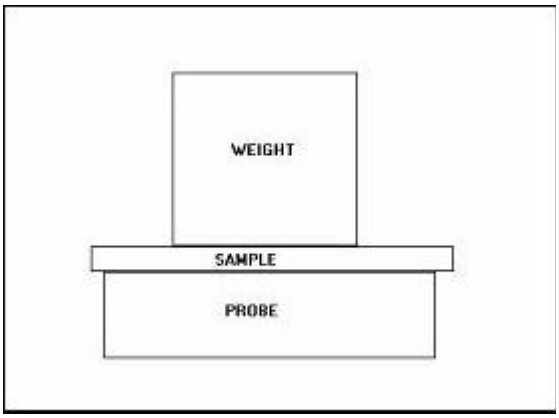

Figure 1. Sample position.

The TC Probe was calibrated using certified standards obtained from the instrument manufacturer: Teflon, Pyrex, and aluminum-filled PDMS. The instrument was calibrated prior to each day's analysis. The calibration standards were run periodically during the sample analyses to verify that the instrument remained calibrated. All samples and standards were analyzed five times and the standard deviation was calculated to determine the precision of the data. The effusivity data were plotted against shim thickness to maximize the instrument parameters relating to heat penetration into the substrate.

RESULTS AND DISCUSSION

The effusivity data were collected using various test durations. The test duration is the time that the temperature change is measured at the probe surface. Figure 2 shows that the test duration time is measured from the start to the stop points noted on the diagram. In this case the test duration is from 0.45 seconds ($\sqrt{0.2}$ seconds) to 0.77 seconds ($\sqrt{0.6}$ seconds) with a ΔT at

the sample/probe surface of 0.37°C. Given the short heating time, the resulting change in temperature is small.

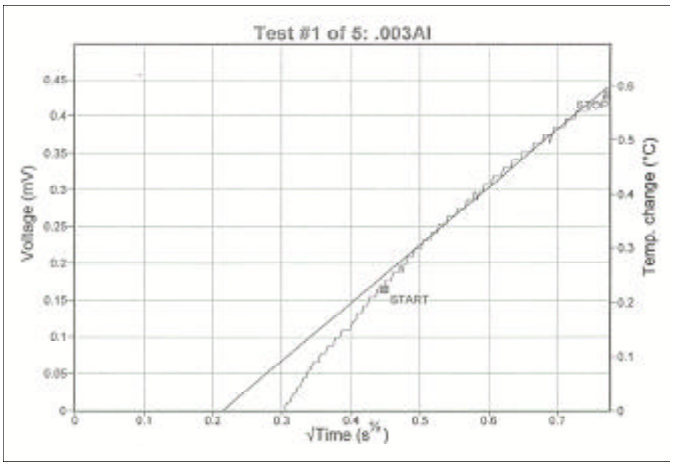

Figure 2. Temperature measurement profile.

Table 1 compares the effusivity data for the various test duration times. Eight samples were tested for each duration. There were three sets of samples. The first, standards, Pyrex (1347 W $\sqrt{s}/m^2$ K), and aluminum-filled PDMS (2078 W $\sqrt{s}/m^2$ K), was selected because the effusivity bracketed the painted Q panel test specimens. The second set was aluminum 2024 and standard Q panel material, with plastic shim stock, ranging from 0.0 to 0.005 in. (0 to 12.75 μm), used to evaluate the degree of penetration of the heat wave through each shim stock thickness. The shim stock was used to represent various coating thicknesses; however, it should be noted that the shim stock, placed between the aluminum panel and probe surface, was not bonded in any way to the aluminum substrate. It is conceivable that some thermal effects could be created by any gaps or voids existing between the shim and substrate. The last set of samples, CQ0069A6 and CG0069A9, was from a series of accelerated environmental paint coatings. The CQ sample was aged under QUV protocol and the CG sample was aged using the GM9540 procedure. The substrate used for the CQ and CG specimens was 2024 aluminum standard Q panel material.

The effusivity data for the standards (see Table 1), show reasonable correlation with their certified values. The Al/PDMS standard averaged 30 W $\sqrt{s}/m^2$ K below its certified value and the Pyrex averaged 82 W $\sqrt{s}/m^2$ K above its certified value. This is attributable to the instrument software calculating a linear curve fit, when, in fact, the calibration curve is not linear in the region of interest. The test duration times of 0.2 and 0.3 seconds produced a lot of scatter in the data, as seen in the large standard deviation. Increasing the test duration time above 0.3 seconds resulted in a steady decrease in the standard deviation with respect to time. Thus, it is advantageous to run the experiment using the longest possible test duration.

Table 2. Test Duration Versus Specimen Effusivity

Test Duration (s)	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	2.0	5.0
Start Time (s)	0.05	0.09	0.1	0.16	0.2	0.3	0.3	0.36	0.42	0.5	1.0
Corr. Coef.	0.945	0.973	0.991	0.998	0.982	0.97	0.995	0.991	0.989	0.988	0.998
Al/PDMS	2140+/-98	2237+/-112	2020+/-64	2088+/-58	2045+/-30	2045+/-30	2043+/-20	2027+/-23	2056+/-36	2019+/-15	2082+/-17
Pyrex	1366+/-28	1474+/-117	1416+/-38	1383+/-32	1442+/-60	1442+/-60	1398+/-32	1433+/-21	1481+/-18	1460+/-10	1406+/-12
Aluminum	2418+/-128	2981+/-66	2779+/-75	2758+/-65	2874+/-30	2954+/-60	2904+/-53	3048+/-27	3188+/-40	3739+/-20	4055+/-18
0.003/Al	481+/-37	782+/-104	1259+/-28	1161+/-47	1312+/-19	1645+/-46	1597+/-11	1731+/-32	2027+/-22	2842+/-14	3605+/-24
0.004/Al	316+/-57	354+/-111	935+/-20	895+/-65	938+/-47	1279+/-24	1306+/-23	1438+/-23	1704+/-21	2479+/-13	3478+/-13
0.005/Al	292+/-79	216+/-139	651+/-22	536+/-27	744+/-31	1053+/-14	1047+/-11	1145+/-18	1328+/-27	2111+/-15	3149+/-39
CQ0069A6	1673+/-85	1396+/-76	1526+/-52	1692+/-78	1698+/-27	2006+/-23	1937+/-56	2179+/-22	2312+/-31	2875+/-19	3518+/-21
CG0069A9	1254+/-71	1079+/-191	1278+/-18	1499+/-85	1612+/-56	1787+/-43	1874+/-29	1994+/-34	2246+/-46	2913+/-22	3581+/-18

The next set of samples analyzed were aluminum and aluminum with plastic shim stock (see Table 1). Figure 3 is a plot of the sample effusivity versus the test duration time. Figure 3 shows that the aluminum panel without shim stock, as expected, had the highest effusivity values for all test duration times. The 0.003-in. (7.62-μm) shim/Al had the next highest effusivity and as the shim stock thickness increased, the effusivity decreased because the heat wave took longer to penetrate into the aluminum substrate, which has a much larger thermal conductivity. This trend was observed at each test duration time. From 0.4 to 0.9 seconds, the difference in effusivity between the aluminum panel and 0.003 in. (0.0762 mm) shim/Al remained relatively constant. As the time increased from 1.0 to 5.0 seconds, the effusivity appears to be converging with the aluminum panel. The same trend can be seen for the 0.004- and 0.005-in. (10.16- and 12.7-μm) plastic shim stock. Thus, as the heating time increased, the heat wave penetrated the shim into the substrate and the effusivity measurement observed was increasingly affected by the aluminum substrate. Test duration times ranging from 0.4 to 0.9 seconds could be used to obtain information relating to environment aging of thin coatings, even though the heat wave did penetrate the shim and pass into the substrate.

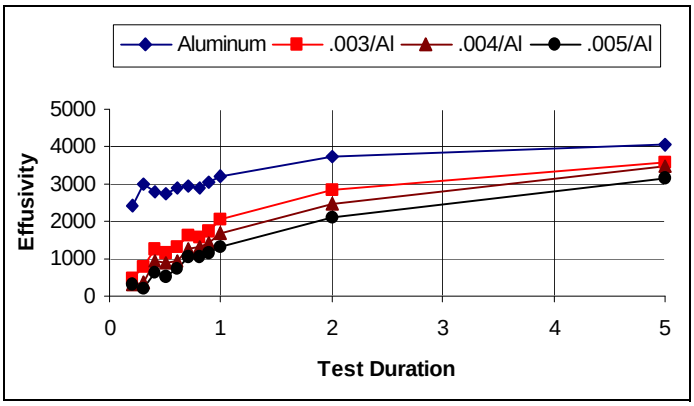

Figure 3. Effusivity, shim and Al vs. test duration.

Samples CG0069A9 and CQ0069A6 both have a solvent-base polyurethane top coat with a solvent base epoxy primer. Both samples were exposed to accelerated environmental aging. The CG sample was aged using GM9540, a cyclic salt spray and 95% humidity exposure, while the CQ was aged using QUV protocol, ultraviolet light radiation. The samples were exposed to accelerated environmental testing to evaluate the effects of polymer degradation and corrosion on the coating. In Figure 4, the effusivity of samples CQ, CG, and aluminum are plotted versus the test duration time. In the range of 0.2 to 1.0 second, the effusivity of CQ on average is 12% higher than that of CG, but above 1.0 second they approach the same value. This is most likely caused by the difference in coating thickness and the effects of environmental aging. Sample CG has an average coating thickness of 76.5 µm (0.003 in.) while CQ has an average thickness of 87.5 µm (0.0034 in.), a difference of 14.4%. The CG coating was not only thinner, but it also had lower effusivity values up to 1.0 second. If the coatings were in fact identical and applied at the same time, it would be expected that the thinner coating would have a greater effusivity owing to the faster heat penetration into the aluminum substrate. This indicates some possible property changes in the coating. Infrared spectrophotometry and differential scanning calorimetry need to be run on these samples to verify changes in the polymer structure. Also, the data need to be normalized for coating thickness if we are to accurately correlate any coating degradation data to environmental aging. As the heating duration increases, the degree of thermal penetration into the substrate also increases, as seen in Figure 4.

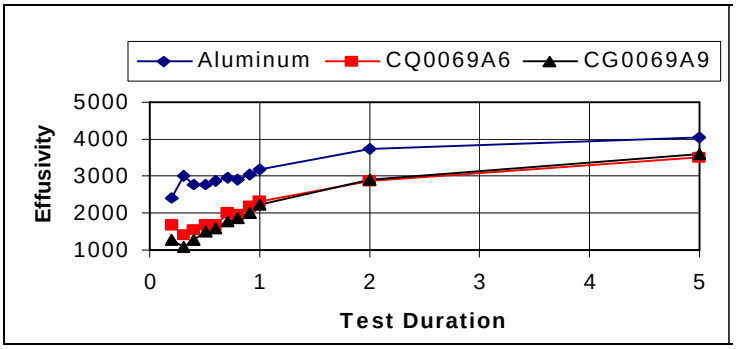

Figure 4. Effusivity, test panels vs. test duration.

CONCLUSION

The data obtained using the Thermal Conductivity Probe show the potential for the development of a non-destructive method to characterize a thin coating. In the range of 0.4 to 0.6 seconds, reasonable effusivity data can be obtained to evaluate thin coatings on a metal substrate. The precision is decent and the effusivity values appear to remain fairly constant. From 0.6 to 0.9 seconds, there is an increase in all the effusivity values, but a second plateau seems to occur and the precision improved. The plastic shim stock data show that there is some heat penetration into the substrate, but the effect appears to be minimal. Caution should be used when evaluating the shim stock data owing to any possible effects caused by no adhesion to the substrate. Subsequent experiments need to be run on bonded shim material to verify the data. Similar results can be seen for the CG and CQ test panels. In comparing the shim stock and coated panel data to the aluminum test panel data, up to a 2.0-second test duration time, the difference in effusivity is almost constant. To accurately compare the coating panel data, the effusivity data need to be normalized to account for variation in the coating thickness.

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